

Hydrogeologic assessment of in situ natural attenuation in a controlled field experiment

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[1] An experiment to investigate the natural attenuation of three volatile organic compounds, toluene, carbon tetrachloride, and tetrachloroethene ($\sim 1\text{--}10\text{ mg L}^{-1}$) was performed in a 3 m deep, sandy aquifer isolated within a 24 m long, 2 m wide, three-sided sheet pile alleyway (hereafter referred to as the gate). A constant flow was maintained in the test volume by pumping a well at the closed end of the gate at 130 mL min^{-1} . The test compounds were introduced to the aquifer using diffusive emitters installed inside 25 cm diameter wells located at the open end of the gate. Monitoring was performed by sampling along six multilevel fences (consisting of 12 sampling points each) ranging in distance from 1 to 22 m from the source wells. A bromide tracer experiment established that there were no significant hydraulic leaks, nor was there any continuous channeling through the gate. Degradation of the test compounds was assessed by mass balance calculations between fences located 1 and 7 m from the source, and the results were compared with degradation rate estimates from snapshot analyses and the analysis of fluxes. There was reasonably good agreement between rates estimated by these different methods. Toluene degraded with a half-life of 58–62 days, carbon tetrachloride degraded with a half-life of $\sim 11\text{--}13$ days, and tetrachloroethene degraded too slowly for a reliable estimate of rate to be made. Transformation products identified in the gate included acetate, possibly from toluene degradation, chloroform, trichloroethene, and *cis*-1,2, dichloroethene. The latter two compounds only appeared in trace quantities and could not be assessed for continuing degradation. However, chloroform degradation was assessed with the snapshot data and using the flux estimates and was found to degrade with a half-life in the range of 10–34 days. No additional chlorinated methanes were detected in the gate, suggesting that the carbon tetrachloride was completely dechlorinated by natural processes within 10 m of the source wells. This experiment demonstrated that degradation of chlorinated solvents occurs naturally at the Borden site but that the ethenes are more resistant to biodegradation than the methanes. In addition, the flux calculations were found to be the most robust in terms of estimating degradation rates. **INDEX TERMS:** 1831 Hydrology: Groundwater quality, 1832 Hydrology: Groundwater transport; **KEYWORDS:** flux, natural attenuation rates, mixed plume, solvents in groundwater

1. Introduction

[2] The processes of natural attenuation are frequently relied upon to limit the spread of organic contaminants in groundwater. Natural attenuation is in use as a remedial strategy at 25% of superfund sites and is the leading remedy for contamination from underground storage tanks [MacDonald, 2000]. Among the most common of the industrial organic pollutants found in groundwater are the petroleum hydrocarbons and chlorinated aliphatics. Within these classes of chemicals the compounds considered most problematical include benzene, toluene (TOL), xylenes and ethylbenzene, carbon tetrachloride (CT), tetrachloroethene (PCE), trichloroethene (TCE), dichloroethenes (DCE), and vinyl chloride (VC). In all of these cases, laboratory studies have shown the chemicals to be degradable

by microorganisms found in aquifers (refer to Wiedemeier *et al.* [1999] for an extensive reference list on this subject). However, most researchers concede that there are considerable difficulties in extrapolating laboratory-based biodegradation studies to the field. Therefore natural attenuation researchers and practitioners look to a growing body of case study reports from industrial and military sites for evidence of in situ natural attenuation of these chemicals [Alleman and Leeson, 1999; Wickramanayake *et al.*, 2000].

[3] In examining the case study literature, it quickly becomes apparent that nearly all the field studies documenting natural attenuation involve well-developed plumes that may extend hundreds of meters in length. Instrumentation is often limited to a relatively small number of monitoring wells that are constructed with long screens. There is generally poor control over the source history (sometimes even the location), and the contaminants migrate in heterogeneous and variable flow systems. A mass balance might

be attempted to prove natural attenuation by comparing contaminant masses crossing monitoring fences located along the flow path at different distances from the source. However, given the above uncertainties, such an attempt is unlikely to succeed. Also, despite the appearance of transformation products or compelling indirect evidence of degradation, there remains some doubt about the proportions of mass disappearance due to various other causes, such as inadequate monitoring, dilution due to dispersion, mixing in wells, matrix diffusion, sorption, and volatilization. Stable isotopes offer considerable promise in helping to distinguish mass losses due to biodegradation from those due to physical processes [Hunkeler *et al.*, 1999; Ward *et al.*, 2000], but they do not provide enough information on their own to permit the calculation of degradation rates. Despite these difficulties the apparent consistency of biodegradation as the chief attenuating mechanism for the lighter petroleum hydrocarbons in aerobic environments has led to a high degree of confidence that natural attenuation is a viable remedial strategy. However, the same confidence cannot be extended to all classes of organic pollutants; recently, a *National Research Council* [2000] committee rated the likelihood of the natural attenuation of chlorinated aliphatic compounds as being low. There remains a need to demonstrate chlorinated solvent natural attenuation in a controlled field setting and to compare approaches for quantifying natural attenuation that might be adapted to less controlled field sites.

[4] The purpose of this experiment was to compare hydrogeological methods of assessing and quantifying the natural attenuation of a plume containing TOL, representing the hydrocarbon class of chemicals, CT and PCE, representing chlorinated aliphatic compounds, in a highly controlled in situ environment. The experiment was performed in a 24 m long, three-sided sheet pile alleyway, hereafter referred to as the gate, which served as a control for concurrent experiments aimed at evaluating sequenced, in situ semipassive technologies [Barker *et al.*, 2000]. With the hydraulics tightly controlled, an experimental setting was established that made it possible to address the second objective of this study: to attempt mass balances and compare the results with biodegradation assessments based on contaminant distribution snapshots and flux differences along the flow path. A further objective was to evaluate the effects of mixed contaminants on degradation behavior.

2. Description of the Field Site

[5] The experiment was conducted at the Canadian Forces Base Borden. The test aquifer was pristine, unconfined, 3 m deep, and underlain by a 6 m thick aquitard. The aquifer comprised a well-sorted, discontinuously laminated, fine beach sand. Borden sand has been characterized extensively; it contains a significant carbonate component that tends to buffer the pH of the groundwater at near neutral values, the organic carbon content is low, on the order of fraction of organic carbon = 0.0002, and the porosity is ~ 0.33 [Ball *et al.*, 1990].

[6] The aquitard comprises an upper silty clay unit that is stiff and blocky for 1.5 m and soft and plastic for 1.75 m. This is underlain by a lower aquitard unit that Morrison [1998] described as a diamict. Aquifer testing, consisting of pumping a well inside the sheet-piled area and looking for a response in a well immediately outside the sheet piles, was conducted to evaluate possible hydraulic connection across the sheet piles. This testing indicated that the aquitard was an effective hydraulic barrier beneath the gate.

[7] The water table was, on average, ~ 0.8 m below ground surface (bgs) but varied between ~ 0.3 and 1.5 m bgs depending on time of year and location in the gate. The site was covered with a 30 m long by 9.2 m wide greenhouse structure consisting of steel tube framing and a flame retardant, vinyl-coated polyester cover. This shelter protected the equipment and instrumentation from the elements, facilitated sampling throughout the year, and prevented direct local recharge due to rainfall or snowmelt, which might have influenced the hydraulics.

3. Methods

3.1. Experimental Design

[8] The experiment was conducted in a three-sided sheet pile box, 24 m long by 2 m wide and ~ 3 m deep (Figure 1). Waterloo Barrier[®] sheet piling was driven into the ground and keyed into the aquitard to break any hydraulic connection between the inside of the gate and the surrounding aquifer. In addition, the joints of the sheet piles were filled with grout, following installation, as a further precaution against contaminant leakage out of the test volume.

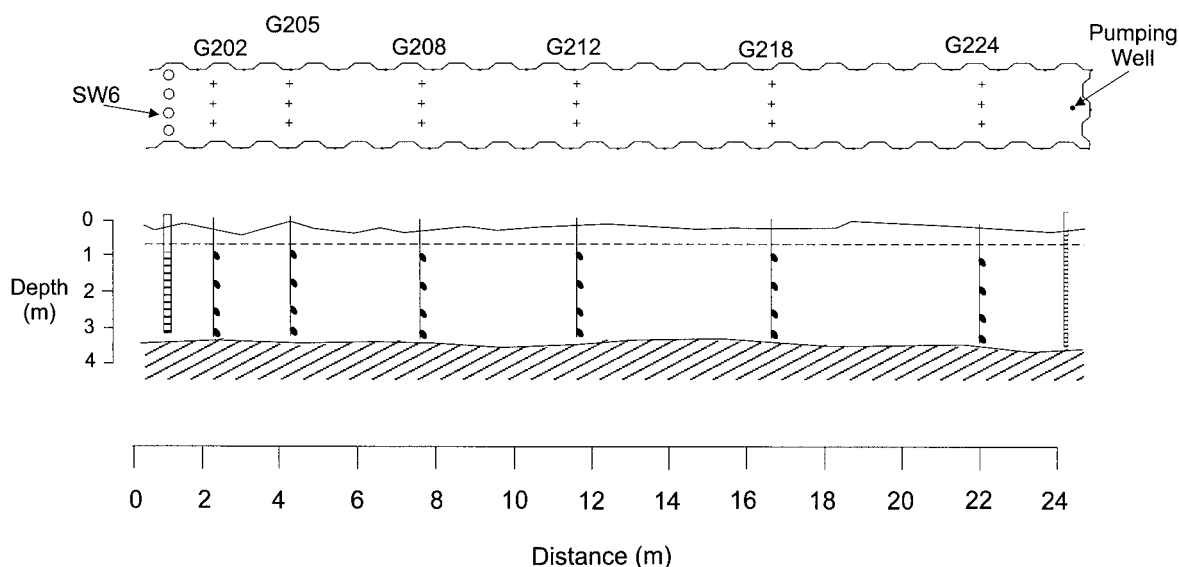


Figure 1. Plan view and cross section of the experimental gate.

The integrity of the seals was assessed throughout the experiment by regular sampling (for volatile organic compounds (VOCs)) of monitoring wells located immediately outside the gate and was found to be satisfactory.

[9] The groundwater flow inside the gate was maintained by continuous pumping of a fully screened 5.08 cm (2 inches) well, located at the closed end of the gate, at a rate of 130 mL min⁻¹. The uniformity of the flow was assessed by releasing 4.6 Kg of potassium bromide tracer at the upgradient end of the gate and tracking its progress over time. The concentrate solution of 9 g of KBr per Kilogram of solution was injected into the source wells at a rate of 10 mL min⁻¹ for a total of 65 hours to create a pulse of ~500 mg L⁻¹ Br⁻. Average linear groundwater velocities were also determined from this experiment and found to be in the range of 8–11 cm⁻¹/day, expressed as fence averages. More details are provided in section 4.

[10] The organic test compounds were released from diffusive emitter devices installed inside four 25.4 cm (10 inches) diameter, fully screened wells located at the upgradient end of the gate [Barker *et al.*, 2000]. Each emitter device consisted of a length (ranging from 10 to 12 m) of 0.4 cm outer diameter (OD), 0.3 mm thick low-density polyethylene (LDPE) tubing coiled around a central PVC frame and lowered into the well. Separate emitters, one dedicated to each test compound (PCE, CT, and TOL), were placed in each source well. The emitters in a given well shared a common support frame. At the tops of the emitters the LDPE tubes were connected to 3.2 mm diameter stainless steel tubes that were, in turn, connected to three 114 L source drums, each dedicated to an individual test compound. The source drums were placed in overpack drums as a precaution against spillage due to leaks. The drums each contained about 1 L of reagent grade nonaqueous phase liquids (NAPL) and ~100 L of water. The liquid mixtures were gently stirred with a drill-adapted mixing rod, and the drums were sealed. Subsequent mixing was performed on a weekly basis without opening the drums. NAPL-saturated water from the drums was circulated through the emitters on a timed cycle of 3 hours pumping followed by 8 hours rest. The solutions passed through the emitter tubes were returned to the drums in closed loops. Occasionally, the drums were reopened, and additional NAPL was added and remixed, as required. The target concentrations, to be achieved in the source wells and in the aquifer, were 2–10 mg L⁻¹ for TOL and 1–2 mg L⁻¹ for PCE and CT. Previous work established that the retardation factors for the test compounds CT, CF, TOL, and PCE in the Borden aquifer were about 1.2, 1.1, 1.2, and 2.7, respectively [Barker *et al.*, 2000].

[11] Multilevel monitors were installed across the gate, in fences, at distances of 0.9, 3.84, 7.27, 11.25, 16.28, and 21.68 m from the source wells and were designated G202, G205, G208, G212, G218, and G224, respectively (Figure 1). Each fence consisted of three monitors designated L, M, or R, depending on whether the device was located on the left middle or right side of the gate (looking toward the pumping well). Each multilevel was constructed from four 3.2 mm (OD) stainless steel (ss) tubes strapped to a central 1.25 cm OD PVC stalk. The ss tubes terminated at depths of 1.2, 1.9, 2.6, and 3.3 m bgs with a fine ss mesh wrapped around the ends to prevent invasion by sand.

3.2. Sampling Methods

[12] Sampling was conducted for a variety of solutes and geochemical parameters. Complete details of the methods and quality assurance and quality control (QAQC) are reported by Barker *et al.* [2000]. Briefly, all samples were collected from the multilevel points using either a peristaltic pump or a 60 mL syringe for suction. The

monitors were purged of a volume equivalent to 3 times the standing water volume of the deepest point (57 mL) prior to collecting samples. Dissolved organic solute samples, including VOCs and organic acids, were collected in 40 mL screw cap glass vials with Teflon-lined septa. The vials were placed in line ahead of the pump to avoid contact with pump head tubing.

[13] Inorganic samples were collected in polypropylene bottles; cations were filtered with 0.45 µm membranes and acidified with nitric acid (10 drops per 60 mL bottle) to achieve a pH of ~2. Anion samples were unfiltered and unacidified. Dissolved oxygen concentrations were measured either with an Orion model 835 meter and a model 083010 probe (for concentrations >0.5 mg L⁻¹) or using the Chemetrics colorimetric method (for concentrations <0.5 mg L⁻¹).

[14] Hydrogen was measured using the method of Chapelle *et al.* [1997]. Three samples were collected from any given location, and the results were averaged for later interpretation. The method precision was about ±0.3 nM.

3.3. Analytical Methods

[15] Non-chlorinated hydrocarbon gases were analyzed using an Hewlett Packard (HP) 5840A gas chromatograph (GC) equipped with a 2 mL sample loop, a 30 m Megabore GS-Q capillary column with helium flowing at 12 mL min⁻¹ serving as the carrier gas, and an oven temperature of 100°C. The injector temperature was 100°C, and the detector, a flame ionization detector, was kept at 200°C. VOCs were analyzed using an HP 5890 GC equipped with a photoionization detector and a Varian Genesis headspace autosampler.

[16] Inorganic anions were analyzed by Water Technology International Corporation (WTI), Burlington, Ontario, Canada, using a Waters Ion Chromatograph equipped with a Waters Series 590 pump, a WISP UK Rheodyne Sample Injector, an IC-Pak A HR column, a 430 conductivity detector, and a Spectra Physics SP4290 integrator. Cations were analyzed at WTI by inductively coupled plasma. Acetate was analyzed by Barringer Labs, Mississauga, Ontario, Canada, by ion chromatography, using a method obtained from the Dionex Ion Chromatograph Series 4500i [Barker *et al.*, 2000].

[17] Method detection limits for VOCs were estimated from calibration curves as described by Devlin [1996]. They were <10 µg⁻¹/L for all VOCs identified in this study. Precision was estimated by comparing the analyses of duplicate pairs. In most cases, precision was in the range of ±15–25%. The exceptions were PCE (±30%) and carbon tetrachloride (±75%). In the latter case the high percentage uncertainty is reflective of the low concentrations in the duplicates collected during the QAQC program rather than the overall quality of the analyses. Since carbon tetrachloride transformed rapidly and was not present in most of the gate, the uncertainty experienced in this compound's analysis was not problematical to interpretation.

[18] Inorganic anions and major cations all had method detection limits of 1 mg L⁻¹ or less and were analyzed with precision of ±10% or less, except for chloride (±15%) and dissolved oxygen (DO) (±40% at concentrations <0.5 mg L⁻¹). Since the concentrations of chlorinated compounds introduced to the gate were quite low in comparison to background chloride, there was little chance for a chloride mass balance, even with a very sensitive and precise analytical technique. Therefore chloride was examined for site characterization purposes only, and the precision experienced was considered acceptable. DO levels <0.5 mg L⁻¹ were considered indicative of bulk anaerobic conditions; no attempt was made to use the measured DO levels for more quantitative purposes.

3.4. Data Reduction

[19] The monitoring program produced a detailed data set of solute concentrations, as a function of time, at each of the multi-level monitoring points in the gate. Average linear groundwater velocities at these points (v) were calculated from

$$v = d/t_{cm}, \quad (1)$$

where d is the distance from the source wells to the monitor (L) and t_{cm} is the time of arrival of the center of mass of a tracer pulse (T). The quantity t_{cm} was estimated by integrating the concentration time curve to determine the total area beneath it and then taking the time corresponding to half that area.

[20] Mass crossing a monitoring point (M) was calculated from

$$M = \int_{t1}^{t2} C \phi A v dt, \quad (2)$$

where C is the solute concentration (ML^{-3}), ϕ is porosity (dimensionless), A is cross-sectional area represented by the sampling point (L^2), t is time (T), and $t1$ and $t2$ are the times corresponding to the beginning and end of a concentration time curve, respectively. The area terms were generated assuming each point represented a rectangular area surrounding it. The rectangular areas were immediately adjacent to each other so that the total cross-sectional area of the aquifer was equal to the sum of the areas represented by the points. Mass crossing a fence was calculated by adding the masses from each point,

$$M_{tot} = \sum_i \sum_j M_{ij}, \quad (3)$$

where M_{ij} is the mass at monitoring point i, j and M_{tot} is the total mass at the fence.

[21] The average concentration at a specified time at a fence was calculated by first determining the solute mass at the fence and then dividing that mass by the solution volume represented by the fence (assuming horizontal flow and unit length in the direction of flow),

$$C_{avg} = \frac{\sum_i \sum_j C_{ij} \phi_{ij} A_{ij}}{\sum_i \sum_j \phi_{ij} A_{ij}}. \quad (4)$$

Since in this experiment the areas represented by the sampling points were all about equal and the porosity of the sand was the same throughout the gate, a good approximation of (4) is the arithmetic average of point concentrations

$$C_{avg} = \frac{\sum_i \sum_j C_{ij}}{n}, \quad (5)$$

where n is the total number of monitoring points on the fence ($=3 \times 4 = 12$). Equations (1) and (4) were incorporated into an algorithm and coded in FORTRAN as the program FENCE [Barker et al., 2000].

4. Results and Discussion

4.1. Tracer Test

[22] The tracer test revealed that average linear groundwater velocities (in stream tubes intersected by the multilevel monitors)

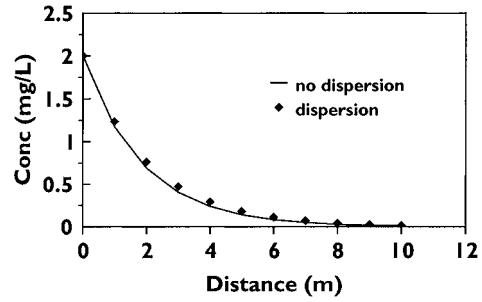


Figure 2. Comparison of steady state concentration profiles for a hypothetical compound with and without dispersion. Parameters used in the simulations were a groundwater velocity of 0.1 m d^{-1} , a dispersivity of 0.21 m , and a reaction half-life of 13 days .

ranged from 5 to $17 \text{ cm}^{-1}/\text{d}$ with an average and standard deviation of $10 \pm 3 \text{ cm d}^{-1}$. Although the average linear groundwater velocity was generally consistent throughout the gate, the fastest rates of migration were frequently associated with the shallowest sampling points.

[23] Longitudinal dispersion was assessed in a separate tracer test in a sister gate constructed immediately next to the current one and with identical dimensions. Instantaneous concentrations at monitoring points on a fence $\sim 12 \text{ m}$ from the source wells were averaged, and the resulting averaged breakthrough curve was fitted with a one-dimensional (1-D) solution of the advection dispersion equation [Devlin and Barker, 1996]. The fence-averaged dispersivity was found to be 0.21 m , corresponding to a relatively small amount of dispersion. In fact, hypothetical degradation rate constants calculated from equations that included dispersion and those from equations that neglected dispersion were $<10\%$ apart (Figure 2). This justifies a simplified analysis of the data and the omission of dispersion terms from the transport equations that follow.

[24] The magnitude of the masses breaking through at the various points revealed no noticeable spacial trend. The average and standard deviation of potassium bromide mass passing any sampling point over the duration of the test (1 year and 1 month) was $425 \pm 325 \text{ g}$; the range was from 0 to 1200 g . This wide range, together with the lack of any obvious spacial trend, suggests that the monitoring point density (two points per square meter, on average) may not have been sufficient to track the mass with the precision necessary for a complete mass balance. Mass balance calculations were performed using FENCE to obtain point-specific breakthrough masses and then adding the masses for each fence. The mass balance at fences G202, G205, G208, G212, and G218 (at G224 higher uncertainties exist because of incomplete breakthrough curves at the end of the test) averaged 4.8 Kg of $\text{KBr} \pm 0.8$ (1 standard deviation, compare to 4.6 Kg KBr injected) or about $\pm 30\%$ at the 95% level of confidence. This level of uncertainty is considered reasonably good for a field experiment, and the available data support the view of a reasonably uniform flow system. There is no evidence of continuous channels conducting disproportionate amounts of solute mass or of physical sinks for solute mass along the gate. Furthermore, the mass balance is sufficient to identify mass losses due to degradation, when degradation is pronounced (as it must be for natural attenuation to be a viable remediation strategy).

[25] The tracer mass balance was reasonably successful in this work, but the $\pm 30\%$ uncertainty in this highly controlled and densely monitored gate illustrates that difficulties should be expected in any attempts to assess natural attenuation on the basis

of mass balances, even in simple hydrogeologic environments, with any but the most detailed monitoring networks.

4.2. Redox Conditions

[26] Prior to beginning the experiment, the gate was found to be aerobic, with DO concentrations on the order of $2\text{--}7\text{ mg L}^{-1}$ at all depths. Background methane was also detected in trace amounts (generally in the range of $10\text{--}30\text{ }\mu\text{g L}^{-1}$ with a maximum of $36\text{ }\mu\text{g L}^{-1}$), suggesting the possibility of microenvironments that were in an anaerobic state or an upgradient source of methane. Nitrate was nondetectable everywhere in the gate, and iron levels were below detection at the majority of sampling points at the outset of the experiment. In the two cases where iron was detected, the concentrations were $<0.5\text{ mg L}^{-1}$; interestingly, they did not correspond to locations where methane levels were highest. Given the initially aerobic condition of the gate, low iron concentrations are not surprising. Most of the iron in the gate likely existed as solid ferric oxides and hydroxides. Sulphate concentrations in the range of $15\text{--}20\text{ mg L}^{-1}$ and an Eh of between $+50\text{ mV}$ and $+300\text{ mV}$ were measured.

[27] Following the addition of the organic pollutants to the gate, anaerobic conditions developed. DO declined to $<1\text{ mg L}^{-1}$ at most points, methane concentrations rose slightly, but sulphate concentrations remained stable. In contrast, dissolved iron concentrations increased to levels between 0.1 mg L^{-1} (the detection limit) and 1 mg L^{-1} in much of the gate and considerably higher in selected locations near the base of the aquifer. At fence G202 the maximum iron concentration was found to be 22 mg L^{-1} . At fences G205 and G208, iron concentrations rose to a maximum of 5 mg L^{-1} . By G212, maximum dissolved iron was about 2 mg L^{-1} , and beyond this fence concentrations remained below 1 mg L^{-1} . These data suggest that, on the scale of the gate, the redox environment was between oxic and sulphate reducing, with the strongest evidence suggesting that iron-reducing conditions were dominant at depth and near the source wells. In order to delineate the dominant regime more precisely, hydrogen concentrations were measured.

[28] The hydrogen measurements were made at the central wells in fences G202, G212, and G224. At G202, hydrogen concentrations were in the range of $2.5\text{--}5\text{ nM}$, characteristic of a sulphate-reducing environment [Chapelle *et al.*, 1995]. Further downgradient, at G212, the hydrogen levels declined to $0.5\text{--}1.5\text{ nM}$, suggesting iron- to sulphate-reducing conditions prevailed, consistent with the elevated iron concentrations and the relatively unchanging sulfate levels that were found. At the end of the gate, G224, the redox environment was similarly split with hydrogen levels between 0.1 and 2 nM . Although these data are not

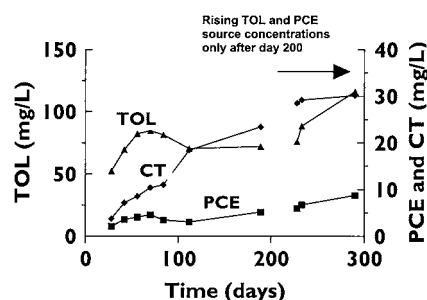


Figure 3. Concentrations of volatile organic compounds over time in source well 6. Abbreviations are as follows: TOL, toluene; CT, carbon tetrachloride; and PCE, tetrachloroethene.

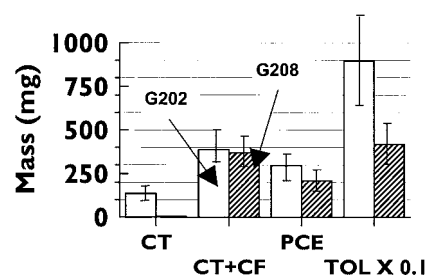


Figure 4. Summary of mass balance calculations. CF is chloroform.

indicative of highly reducing conditions, they do suggest an environment between G202 and G205 that could support dechlorinating microorganisms.

4.3. VOC Sources

[29] In all cases the VOC concentrations in the source wells were at levels considerably higher than targeted (see Figure 3) (targets were $2\text{--}10\text{ mg L}^{-1}$ TOL and $1\text{--}2\text{ mg L}^{-1}$ for CT and PCE), indicating that the LPDE tubing lengths in the emitters were longer than required. The design problems have since been overcome, and an account of the improved method is given by Arildskov and Devlin [2000]. Despite the greater mass delivery from the emitters the source wells delivered very close to the targeted concentrations to the aquifer because of the compensating effect of lower than expected flow through the well screens. Subsequent work indicated that the wells were insufficiently developed to transmit water at the expected rates.

[30] For the first 200 days of the experiment the PCE and TOL diffusive emitters exhibited no consistent trend in the source wells' concentration changes. In contrast, CT concentrations rose by a factor of ~ 3 in the source wells over this time (Figure 3). It was fortunate that the nonideal emitter performance occurred with CT because, as will be discussed in detail in section 4.4, this compound and its transformation products were biodegraded completely to nonchlorinated species quite rapidly by the end of the experiment. So a simple and well-defined source function was not essential to establish the role of natural attenuation in the disappearance of these compounds. After ~ 200 days the mass release rates of TOL and PCE began to increase, possibly because of changing polymer properties resulting from long-term contact with the VOCs. Therefore, for the purposes of simplicity in the mass balance calculations, only the mass released prior to day 200 was considered.

4.4. VOC Mass Balances

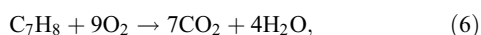
[31] Since the concentrations in the source wells were not representative of the concentrations that developed in the aquifer, the input masses for mass balance calculations were derived from less detailed concentration time curves at the first monitoring fence, G202, rather than the source wells themselves. Mass input over the interval between days 14 and 88 was calculated to take advantage of the relatively constant input (source well concentrations) during that period. In order to remove retardation from the analysis of fence G208 data, sufficient time was allowed for all compounds except PCE to arrive at G208 before integrating the curves (i.e., the transient period of mass transport was allowed to pass). PCE traveled at a retarded rate that precluded waiting for complete breakthrough. As a result, the mass balance for PCE was negatively biased at G208, as will be shown. The integration at G208 was carried out for the interval between days 112 and 238

and then scaled to a 74 day period by multiplying the total calculated mass by 0.587 ($= 74/(238-112)$). Because sources were delivering mass at a constant rate during this time, i.e., the first 200 days for TOL and PCE, this type of scaling correction is considered reasonable. The differences between masses calculated from G202 and G208 were attributed to degradation.

[32] The mass balance calculations clearly showed that CT was degraded rapidly after entering the gate; it was detectable at G202 (maximum $>1000 \mu\text{g L}^{-1}$) but was never above the limit of quantification ($23 \mu\text{g L}^{-1}$) at G208 (Figure 4). This finding is consistent with other work that has been conducted in the same aquifer. *Devlin and Müller* [1999] found that CT was rapidly transformed in a sulphate-reducing environment in the Borden aquifer. They further found, on the basis of a characteristic chloroform (CF) to carbon disulphide (CS_2) ratio of 2, that the transformation was likely to have been abiotic and related to the ongoing precipitation of amorphous FeS in the aquifer. A similar environment might have existed in this experiment; a sulphate-reducing environment near the source wells could have been stimulated by the addition of organic carbon (in the form of toluene) potentially reducing sulphate ($15\text{--}20 \text{ mg L}^{-1}$ background) and precipitating FeS with iron naturally present in the aquifer material. However, sulfate concentrations did not significantly decline during the experiment, so sulfate reduction was at best only patchy. Also, CS_2 was only detected in trace quantities early on in the experiment and never approached the characteristic ratio with CF. In fact, the mass balance indicates that in the early part of the experiment, CF was by far the dominant, perhaps the sole, transformation product (Figure 4). *Devlin and Müller* [1999] found a similar CF product dominance in their most biologically active (sulphate reducing) systems. So, while abiotic reactions other than the one with FeS cannot be entirely ruled out, the available data are consistent with a CT transformation that was biologically driven.

[33] The mass balance on PCE indicated that slightly less mass reached G208 than was introduced at G202. This is attributable to the slow transport of PCE through the gate and the arrival of the plume front during the integration period. In spite of this the difference is within the $\pm 30\%$ error bars for a mass balance determined from the bromide tracer test. Therefore the apparent mass loss cannot be attributed to degradation. The lack of detectable transformation products during the early stages of the experiment was further evidence that PCE was not degrading.

[34] Toluene underwent some mass loss between G202 and G208. In this case the loss was $\sim 50\%$, indicating that biodegradation was taking place. Given a background DO of about 3 mg L^{-1} , a flow rate of 138 mL min^{-1} through the gate on average, and the following stoichiometry for the complete mineralization of toluene,



there was more than enough oxygen available (1.4 mol or 45 g over 74 days) to degrade all the toluene that passed G202 (0.1 mol or 9.1 g over 74 days). It is expected that dissolved organic carbon and natural organic carbon in the aquifer contributed to some oxygen removal from groundwater in the gate. However, the natural organic carbon in the Borden aquifer is known to be low [*Ball et al.*, 1990], so this oxygen sink may not explain the toluene persistence. An alternative explanation is that the mass distribution across the gate was nonuniform (Figure 5). Concentrations within

various streamlines varied from a few micrograms per liter to 15 mg L^{-1} , but the DO (more evenly distributed at $\sim 3 \text{ mg L}^{-1}$) was only sufficient for the degradation of $\sim 1 \text{ mg L}^{-1}$ along any streamline. Thus some streamlines rapidly became anoxic, slowing further TOL degradation by forcing it to occur anaerobically or halting it completely. Notably, acetate was detected at the base of G212 in concentrations of $75\text{--}85 \text{ mg L}^{-1}$; although these concentrations are too high to be attributable entirely to a TOL source, the acetate may have originated, in part, from TOL biodegradation.

[35] If the degradation reactions are assumed to be pseudo-first-order, then the changes in mass between the two fences (G202 and G208) can be used to calculate degradation half-lives. These calculations indicated that CT and TOL degraded with half-lives of 13 and 58 days, respectively (Table 1). As discussed above, no CF or PCE degradation was discernible.

4.5. Snapshots

[36] The mass balances tell only part of the story because the calculations were limited to times when, and fences where, transient transport effects and source variations could safely be neglected. This limited the analyses to fences near the upgradient half of the gate and relatively early times in the experiment. In order to assess natural attenuation over the entire gate, and at later times, snapshots of contaminant distributions were compared from days 238 and 339. These times are significant because, as will be shown, several important changes occurred in the transformations of chlorinated compounds during this 100 day interval.

[37] Prior to day 238, the only degradation reactions that appeared to be occurring were those of CT to CF and TOL biodegradation. There were no indications, from the appearance of transformation products or on the basis of the mass balance calculations, that either CF or PCE was undergoing any degradation. By day 337 the distribution of CF had changed remarkably (Figure 6). No CF was detected beyond G205 despite the increases in concentrations of CT in the source wells up to day 200. Furthermore, no chlorinated methane transformation products were detected in the groundwater, establishing that CT was being completely dechlorinated within 5 m of the gate. Since

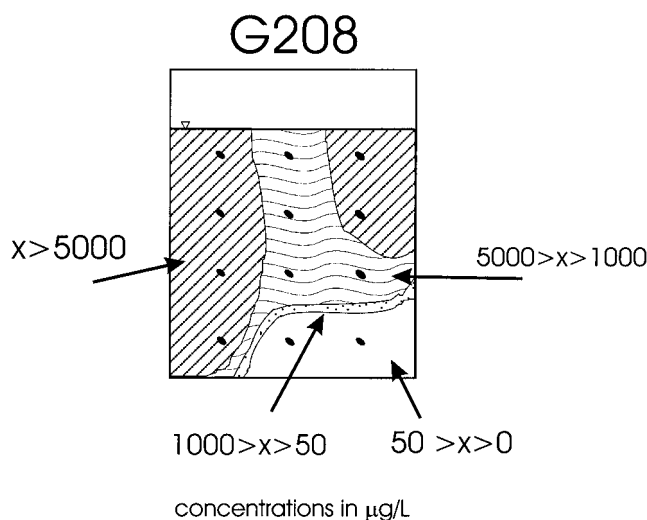


Figure 5. Cross section (flow out of the page) of toluene concentrations at fence G208 on day 112.

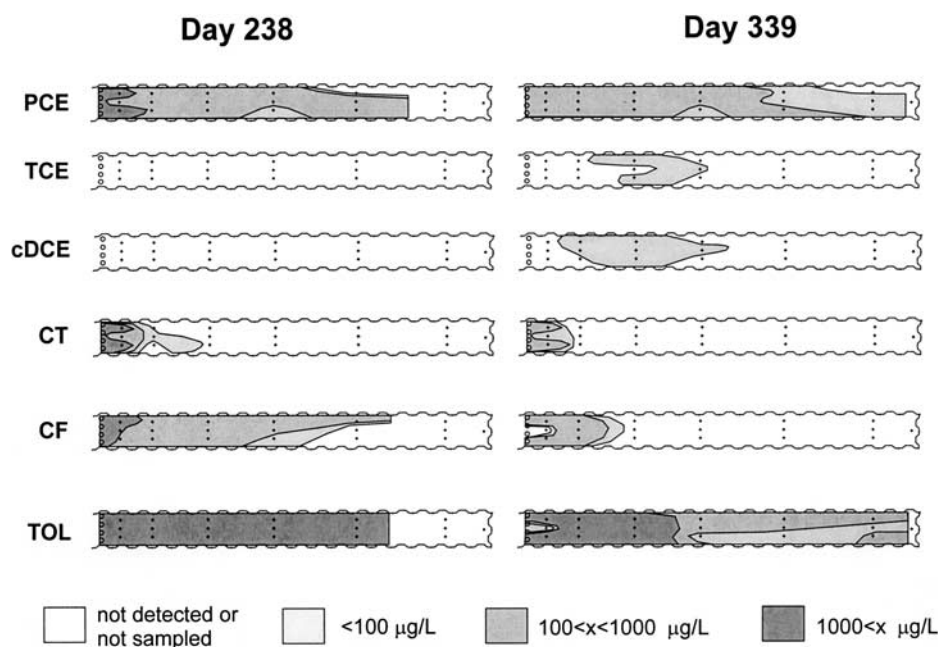


Figure 6. Snapshots of contaminant distributions on days 238 and 339 of the experiment.

there are no known abiotic processes that could account for this complete dechlorination, biodegradation is indicated as the important attenuating process.

[38] The PCE concentrations at the monitors did not change substantially between days 238 and 339, but traces of two transformation products appeared in the central part of the gate (G205–G212): TCE and *cis*-DCE (cDCE) (Figure 6). Neither of these compounds accumulated to concentrations that made them detectable in the mass balance calculations, but their presence demonstrates that reductive dechlorination of PCE was occurring slowly by the end of the experiment. No vinyl chloride (VC) was detected in the groundwater, suggesting that degradation beyond cDCE was not occurring. Alternatively, VC concentrations may have been too low to detect since its precursor, cDCE, was only present in trace quantities. The lack of detectable VC was consistent with results of laboratory microcosms performed with aquifer material from the site and with the results of a concurrently running anaerobic bioremediation experiment conducted immediately next to the current experiment [Barker *et al.*, 2000]. From the location of the first appearance of transformation products (~ 5 m from the source) the time of their appearance (>238 days and <337 days) and the retarded solute velocities in the gate (~ 0.03 m d $^{-1}$ PCE and 0.1 m d $^{-1}$ CF), minimum acclimation times for the degradation of these two chemicals in situ are estimated to be 100 days for PCE and 200 days for CF.

[39] TOL concentrations were uniformly >1 mg L $^{-1}$ at all sampled points on day 238 but declined to <0.1 mg L $^{-1}$ in some locations beyond G208 by day 339 (Figure 6). Given that there were no sources of oxygen to the downgradient regions of the gate (other than minimal diffusion from the surface), the toluene disappearance must be due to anaerobic biodegradation. The electron acceptors likely to be driving this transformation include ferric iron and sulfate, based on the assessment of redox conditions. However, since sulfate concentrations appeared to remain stable in the gate, iron reduc-

tion is indicated as the principle process driving the toluene transformation. Under the conditions of the Borden aquifer (carbonate rich with pH ~ 7 –8), reduced iron might be expected to precipitate as FeCO $_3$ and Fe(OH) $_2$. Equilibrium calculations performed with MINTEQA2 [Environmental Protection Agency, 1991] indicated that aqueous Fe $^{2+}$ concentrations in the range of 4 mg L $^{-1}$ with a solution pH of between 7 and 8 should be expected. These calculations are consistent with our observations, supporting the view that iron reduction was occurring.

[40] In addition to providing an intuitive grasp of the stages of natural attenuation, snapshots can provide the quantitative information needed for modeling. The natural attenuation literature contains many references to the use of plume snapshots, usually along the central longitudinal axis, to quantify degradation. The approach treats the plume as a 1-D or 2-D entity and fits a solution to the steady state advection-dispersion equation, with first-order decay, to the concentration profile. From the fitted curve an estimate of the pseudo-first-order rate constant can be obtained [Wiedemeier *et al.*, 1999]. In this experiment, concentration profiles for TOL or PCE could not be meaningfully fit with simple analytical solutions because of the variations in the source concentrations at late time; profiles did not resemble first-order curves. This scenario is likely to be typical of real sites, highlights a limitation of snapshot analysis, and suggests that caution must be exercised in the assumption of constant sources when estimating degradation rate constants [Wilson *et al.*, 2000]. Fortunately, in this experiment the CT source stabilized at late time (after day 200) making CT profile analysis possible.

[41] The 100 day interval between days 238 and 339 was sufficient to flush about (100 days)(0.1 m d $^{-1}$)/1.23 \Rightarrow 8.1 m of the gate with CT-contaminated water from the stabilized source. Since CT reacted rapidly, it was always attenuated before G208, the fence located 7 m from the source. Thus the CT profile appeared to remain at or near steady state at

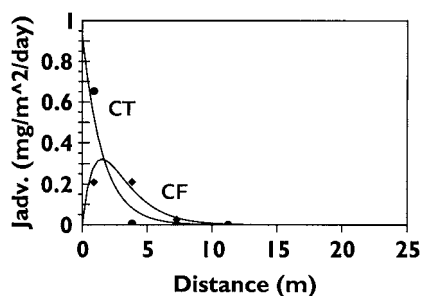


Figure 7. Fitted and actual fence-averaged concentrations of CT and CF along the gate on day 339.

late time. The equation describing 1-D transport of a reacting solute, neglecting dispersion, is

$$\frac{\partial C}{\partial t} = -\frac{v}{R} \frac{\partial C}{\partial x} - \frac{k}{R} C, \quad (7)$$

which leads to the steady state equation

$$C = C_0 \exp\left(-\frac{k}{v}x\right). \quad (8)$$

Here x is distance from the source (M, L^{-3}), k is pseudo-first-order rate constant (T^{-1}) and R is the retardation factor (dimensionless). Using (8) Barker *et al.* [2000] calculated the rate constant for maximum fence concentrations on day 339. From this the half-life ($t/2 = 0.693/k$) was calculated to be 11 days. The same half-life was calculated using fenced-average concentrations from days 238 and 339 (Figure 7). This value compares well with that obtained from the mass balance calculation (Table 1).

[42] If the CT fence-averaged concentration profile was at steady state, then there is some justification for extending the analysis to CF, the transformation product. Although the CF profile on day 339 may not strictly have achieved steady state (biodegradation of the compound was occurring more rapidly at the end of the test than the beginning), the source was well defined (coming from CT). Also, since the profile was receding, any estimated half-life would be conservatively large. The transport equation for the CF transformation product, neglecting dispersion and assuming CF was the only direct transformation product of CT, is

$$\frac{\partial D}{\partial t} = -\frac{v}{R_2} \frac{\partial D}{\partial x} - \frac{\lambda}{R_2} D + \frac{Fk}{R_2} C, \quad (9)$$

where D is concentration of CF, C is concentration of CT, R_2 is retardation factor of CF, k is pseudo-first-order rate constant for CT

disappearance, F is a conversion factor that accounts for stoichiometric coefficients and/or branching pathways (since we observed CT transforming only to CF, with a reasonable mass balance, $F = 1$ in this case) and molecular weights (if concentrations are expressed on a mass rather than molar basis, the factor $F = (W)/(W_p)$, where W is the molecular weight of the product (CF), W_p is the molecular weight of the parent (CT) and λ is the pseudo-first-order rate constant for CF transformation. Substituting (8) into (9) and assuming steady state,

$$D = \frac{FkC}{\lambda - k} \left[\exp\left(-\frac{k}{v}x\right) - \exp\left(-\frac{\lambda}{v}x\right) \right]. \quad (10)$$

Fitting (10) to the day 339 CF profile produced a half-life for CF degradation of ~ 10 days. Comparing this result with that from the mass balance calculations (no demonstrable degradation), it is apparent that CF degradation intensified considerably toward the end of the experiment (Table 1).

4.6. Flux Calculations

[43] Another strategy for assessing and quantifying natural attenuation is to calculate the solute fluxes across the fences and look for systematic declines along the flow path [e.g., Wilson *et al.*, 2000]. Since fluxes are time and area normalized, direct comparisons are possible, in principle, between fences of equal area at opposite ends of the gate or even within a plume of varying lateral and vertical dimensions. As discussed in Section 4.5, in reference to the snapshot data, such comparisons are complicated by the rising source concentrations of some compounds after day 200, but this point will be taken up later. FENCE was used to estimate the total mass of each organic compound that crossed each monitoring fence over the monitored intervals of the experiment. Then, the advective fluxes (J) (in units of $M/(L^2T)^{-1}$) were determined from

$$J = \frac{M_{cum}}{A\Delta t}, \quad (11)$$

where M_{cum} is the cumulative mass advected across a fence (M), A is the cross-sectional area of the fence (L^2 , 6 m^2 was used in these calculations), and Δt is the time interval over which the cumulative mass was calculated (T). For example, fence G208 was sampled between days 70 and 339. Over this period, 135 g of TOL were estimated to have crossed the fence. During this interval the first appearance of TOL at G208 was on day 70, so the total time TOL was considered to be crossing G208 was $339 - 70 = 269$ days. The calculated flux of TOL at G208 during this time was $84 \text{ mg}^{-1} (\text{m}^2 \text{ d})^{-1}$ (Figures 8 and 9).

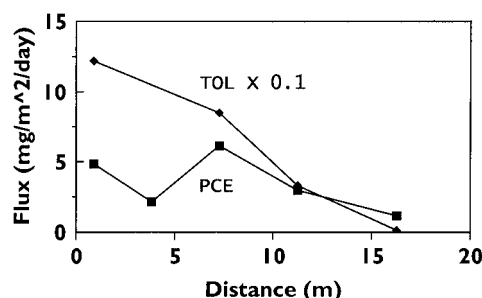


Figure 8. Flux of PCE and TOL as a function of path length through the gate.

Table 1. Summary of Half-Lives Estimated by Three Methods^a

Compound	Half-Lives, days		
	Mass Balance	Concentration Profiles	Flux Profiles
PCE	NT	ND	NT
CT	13	11	11
CF	NT	10	34
TOL	58	ND	62

^a Abbreviations are as follows: PCE, tetrachloroethene; CT, carbon tetrachloride, CF, Chloroform; TOL, toluene; NT, no measurable transformation; and ND, not determined.

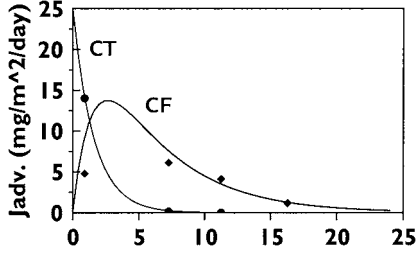


Figure 9. Flux of CT (circles) and CF (diamonds) averaged over the experiment (day 70 onward) and the model fits (curves).

[44] A quick inspection of Figures 8 and 9 reveals that of the four compounds considered, TOL, CT, and CF, have steadily declining fluxes with distance from the source wells. In contrast, the PCE flux is essentially constant along the gate, up to fence G212, indicating that little or no degradation of this compound was occurring and that the slight rise in source strength at late time did not unduly affect the analysis. The slight decline in flux at G218 occurs because the main solute front has not actually arrived there yet. PCE migrates with a retardation factor of ~ 2.7 , so after flushing at 0.1 m d^{-1} (retarded velocity of $\sim 0.03 \text{ m d}^{-1}$) for 337 days, the solute front only traveled 12.5 m. The PCE mass beyond this distance originated from an early trial of the diffusive emitters (PCE was the only solute released in this trial) before the onset of the experiment proper.

[45] The flux values can be used to estimate degradation rates in the same way that concentration profiles were used. The difference in the two approaches is that while concentration profiles are based on snapshots of contaminant distribution and may lead merely to instantaneous degradation rates, fluxes (as calculated in this paper) are based on time-integrated data and lead to degradation rates averaged over a longer term. It is worth noting that others have used snapshot data to estimate fluxes; this sort of data treatment has the same limitations related to short-term fluctuations in source strength, or other transient phenomena, as the snapshot analysis mentioned in section 4.5 [Wilson *et al.*, 2000]. The flux equation for an advecting solute (again without dispersion) undergoing first-order degradation is

$$J_{\text{tot}} = qC - \left[-\phi R \int \frac{k}{R} C dx \right]. \quad (12)$$

C is concentration at distance x from the source (M/L^{-3}), q is the Darcy flux (L T^{-1}), R is the retardation factor (dimensionless), ϕ is porosity (dimensionless), C_0 is concentration at the source, k is pseudo-first-order rate constant (T^{-1}), and v is average linear groundwater velocity (L T^{-1}). At steady state, $J_{\text{tot}} = 0$, and (8) describes C as a function of x . Substituting (8) into the integral term in (12) and solving yields

$$J_{\text{tot}} = 0 = qC - qC_0 \exp\left(-\frac{k}{v}x\right). \quad (13)$$

The three terms in this steady state equation are the total flux, J_{tot} , the advective flux, $J = qC$, and the reactive flux, $qC_0 \exp(-kx/v) = J_0 \exp(-kx/v)$. Therefore (13) can also be written

$$J = J_0 \exp\left(-\frac{k}{v}x\right). \quad (14)$$

Equation (14) relates the advective flux, which can be estimated from field data as described above, to the reaction rate constant, k . Equation (14) was fitted to the field flux data by Barker *et al.* [2000], and they found that CT was degrading with a half-life of 11 days (Figure 9) in agreement with the snapshot analysis presented in section 4.5. TOL was found to be degrading with a half-life of 62 days; PCE was found not to be degrading. These results compare favorably with those from the mass balance calculations (Table 1).

[46] Since CF was not released directly into the gate, but formed from the degradation of CT, another equation had to be derived to describe its flux. Beginning with (12), modified to contain a source term for the production of CF from CT (again neglecting dispersion and assuming CT degrades entirely through CF),

$$J_{\text{tot}}^{\text{CF}} = qD + \left[-\phi FR_2 \int \frac{k}{R_2} C dx \right] - \left[-\phi R_2 \int \frac{\lambda}{R_2} D dx \right], \quad (15)$$

where the superscript on the flux term, J_{tot} , indicates the compound to which the flux applies, D is concentration of CF, C is concentration of CT, k is pseudo-first-order rate constant for CT disappearance, and λ is pseudo-first-order rate constant for CF transformation. The first term on the right is the advective flux of CF; the second term is the source term for the production of CF from CT, in which C is obtained from (9). The third term is the sink term for the transformation of CF, in which D is obtained from (10). Now (15) can be rewritten

$$J_{\text{tot}}^{\text{CF}} = qD + qFC_0 \exp\left(-\frac{k}{v}x\right) + \frac{qC_0 Fk\lambda}{(\lambda - k)} \cdot \left[\frac{1}{\lambda} \exp\left(-\frac{\lambda}{v}x\right) - \frac{1}{k} \exp\left(-\frac{k}{v}x\right) \right]. \quad (16)$$

We are interested in the steady state equation, i.e., $J_{\text{tot}} = 0$, so (16) becomes

$$J^{\text{CF}} = J_0^{\text{CT}} F \left\{ \frac{1}{\lambda - k} \left[\lambda \exp\left(-\frac{k}{v}x\right) - k \exp\left(-\frac{\lambda}{v}x\right) \right] - \exp\left(-\frac{k}{v}x\right) \right\}. \quad (17)$$

Fitting (17) to the measured flux data (Table 2) and assuming the half-life for CT degradation to be 11 days, as determined above, the half-life for CF degradation is estimated to be 34 days (Figure 9). This value is larger than that obtained from the snapshot profile because the CF plume was receding over the time the cumulative masses were calculated; the snapshot data only reflected the final plume span. Despite the variation, half-lives of 34 and 11 days only represent a difference in the gate of about $((34 - 11) \text{ days}) \times 10 \text{ cm d}^{-1} \Rightarrow 2.3 \text{ m}$, a relatively small distance. The flux-based half-life may be considered the more conservatively large of the two estimates. However, to some extent this conservatism might be offset by the increasing source strengths at late time.

[47] The effect of an increasing source strength on a flux-based degradation rate constant, such as discussed above, is to positively bias the parameter. It was pointed out earlier that the PCE flux profile was not unduly affected by the source variations; now the same can be shown for TOL, which experienced the largest late time increase in source strength (Figure 3). Over the first 200 days of the experiment the TOL concentration in source well 6 averaged 73 mg L^{-1} (recall that much lower concentrations developed in the aquifer outside the

Table 2. Summary of Fluxes at Each Monitoring Fence

Distance from Source, m	Fluxes, mg m ⁻² d ⁻¹			
	PCE	TOL	CT	CF
0.9	4.84	12.20	14.00	4.77
3.84	2.13
7.27	6.13	8.50	0.13	6.12
11.25	2.96	3.30	0.00	4.10
16.28	1.15	0.13	...	1.16

source wells, but proportional changes between the two regimes are expected). Assuming this source strength was maintained for the entire experiment (~300 days), the flux of TOL from the well would have been

$$J = \frac{CQ\Delta t}{A\Delta t} = \frac{(73\text{mg/L})Q}{A} = 73 \frac{Q}{A}, \quad (18)$$

where Q is the flow rate through the well ($L^3 T^{-1}$). However, over the last 100 days of the experiment the concentration rose nearly linearly to a maximum of 116 mg L⁻¹. Thus the average concentration over the last 100 days can reasonably be represented as $(73 + 116)/2 = 94$ mg L⁻¹. Now a revised total flux over the 300 day experiment can be determined

$$J = \frac{(73\text{mg/L}^{-1})Q(200\text{ days}) + (94\text{mg/L}^{-1})Q(100\text{ days})}{A(300\text{ days})}$$

$$J = 80 \frac{Q}{A}. \quad (19)$$

The difference between the two estimates is <10%, establishing that the changing source had a minimal effect on the fluxes averaged over the last hundred days and hence the rate constants (and half-lives) for that period.

5. Summary and Implications

[48] An initially aerobic section of aquifer became anaerobic in the presence of TOL, CT, and PCE. Within a few meters of the sources the redox environment became iron reducing to sulphate reducing. The development of anaerobic conditions likely resulted from oxygen consumption in the degradation of TOL. Although sufficient oxygen was introduced to the gate to degrade all the toluene, the mass loading of the organic compound was not uniform across the gate, resulting in oxygen shortages in some stream tubes. The presence of acetate in the gate suggests that TOL was degrading anaerobically. Since anaerobic conditions are a precursor for reductive dechlorination, the mixture of hydrocarbons and chlorinated solvents in the plume appears to have been beneficial in this respect.

[49] This experiment showed that natural attenuation of low mg L⁻¹ concentrations of CT, CF, and TOL occurred rapidly and within a short distance of the source (<18 m). In the absence of any physical sinks for the contaminants (demonstrated in the tracer test) and the lack of any creditable abiotic reactions, the mass losses were probably due primarily to biodegradation. Over the first 238 days of the experiment, there was evidence of CT and TOL degradation (mass balances) but not of CF or PCE. At some time after day 238 and before day 339 both CF and PCE began to

degrade. This result establishes a minimum in situ adaptation time of ~100 days for PCE and ~200 days in the case of CF for the onset of reductive dechlorination.

[50] TOL and CF initially penetrated the gate most or all of its length. In both cases the plumes subsequently receded; in the case of CF the recession resulted in a final plume length of <10 m (from a maximum of >20 m). This manner of plume evolution might be expected where in situ microorganisms adapt to the presence of contaminants, utilize them, and then grow causing increased mass loss rates. Plume recession begins once the degradation rates exceed the influx rates. Although this type of evolution is not a complete surprise, this study is among the first to demonstrate it for chlorinated solvents, in situ, in a highly controlled way.

[51] At the end of the test, PCE proved to be the most recalcitrant compound. This result is consistent with decades of evidence that chlorinated ethenes do not attenuate quickly in groundwater. Nevertheless, PCE did undergo some transformation, as indicated by the production of trace quantities of TCE and cDCE, but the rate was too slow to be observable by any of the fence-monitoring techniques attempted here. This result demonstrates that the mere presence of degradation products is not sufficient to infer significant rates of natural attenuation.

[52] In this experiment, degradation had to proceed with a half-life on the order of 60 days or less to be quantifiable. Such a half-life corresponds to a travel distance of only a few meters; therefore degradation must be quite rapid to be detectable by the methods tested in this study.

[53] Mass balances, concentration profiles, and flux profiles were examined to evaluate natural attenuation in the gate. To perform an ideal mass balance, a parcel of plume must be tracked as it passes two fences, and any mass losses must be calculated. The larger the parcel the more reliable the estimated degradation rate. Although this is a preferred approach in theory, it was found to be a time-consuming method in practice that imposed limitations on which data could be considered.

[54] Concentration profiles were found to be limited by variations in source strength. They reflect instantaneous concentration distributions that are sensitive to short-term fluctuations. Therefore it is critical that the plume be stabilized before applying this method.

[55] The most robust method tested here, and the preferred method, was the one based on flux calculations. Fluxes can be determined for different time intervals and at different fences and compared directly. This has the potential of greatly facilitating the analysis and shortening the data collection time. However, because it is based on time-integrated data, the flux-based method produces rate constants that reflect time-averaged behavior not the most current condition. In spite of the differences all three methods provided similar estimates of degradation half-lives when the plumes were at or near steady state.

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